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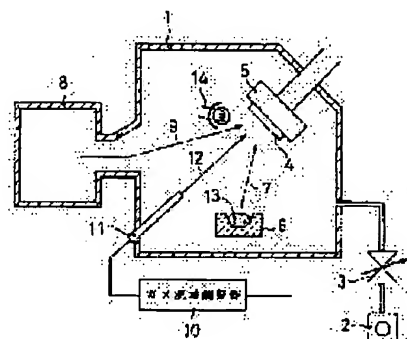
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## (54) TI-RARE EARTH ELEMENT-N ULTRA-HARD COMPOUND FILM AND METHOD FOR FORMING THE FILM

(57)Abstract:

PURPOSE: To obtain the subject ultra-hard compound film having excellent surface hardness, abrasion resistance and sliding property by using one or several kinds of elements selected from Ti, N and rare earth elements constituting the ultra-hard compound in the form of an ion beam, using the remaining elements in the form of a beam of metallic vapor or a gas containing the elements and combinedly irradiating a substrate with both beams.

CONSTITUTION: The following process is an example of the production process. A vacuum film-forming chamber 1 is evacuated to 10-Pa with a vacuum pump 2. NH<sub>3</sub> gas adjusted to 2.0 SCCM by a flow-controller 10 is introduced through a nozzle 11 in the form of a beam 12 and the film-forming chamber 1 is maintained to 4×10<sup>-4</sup>Pa by adjusting a pressure control valve 3. A substrate plate 4 (e.g. steel plate) held with a holder 5 is heated at 300°C with a heater 14. Ti metal 13 in a metal evaporation source hearth 6 is melted and evaporated by electron beam heating and radiated to the substrate 4 in the form of Ti metal vapor 7. At the same time, Dy ion beam 9 generated by an ion source and an ion accelerator 8 is irradiated to the substrate 4 to obtain the subject compound film containing 0.5-20atom% of the rare earth elements.



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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the nature compound film of Ti-rare-earth-elements-N system superhard, and its formation method. in more detail Metal industry, the tool used by the machine and the process industry, and the component part used for various equipments, It is related with the method of forming a coating film on a sliding material-list side, and forming the nature compound film of Ti-rare-earth-elements-N system superhard and this film which have improved the performance of the degree of hardness of a material-list side, abrasion resistance, and a sliding property using the ion mixing method.

[0002]

[Description of the Prior Art] Conventionally, as hard and abrasion resistance formed on substrates, such as this kind of metal, and a sliding nature coating film, the thin film of compounds, such as Ti-N, Ti-C, etc. which were formed on the substrate of PVD or CVD, is known.

[0003] Although formed by the same method as \*\*\*\*\*, the thin film of compounds, such as these Ti-N and Ti-C, is as follows as an example of representation of PVD coating among the aforementioned methods, if the case of formation of the Ti-N film to the substrate top by the hollow cathode electric discharge (HCD)-ion plating method currently performed more widely than before is explained.

[0004] First, the equipment used for PVD is explained. Drawing 8 shows a HCD ion plating system, a shows a vacuum membrane formation room among drawing, and the inside of this vacuum membrane formation room a is connected to vacuum pump b. The substrate of the product made from a metallic material mainly by which coating is presented with c, and d Moreover, metal evaporation-source Haas, The metal material (here Ti) and f which evaporate e A hollow cathode electron gun, The power supply for electric discharge to which g impresses voltage to the hollow cathode electron gun f and metal evaporation-source Haas d, the nozzle for which h passes an electron beam and iN<sub>2</sub> gas, N<sub>2</sub> gas by which a part of j was ionized, and k show the bias power supply which impresses voltage to Substrate c.

[0005] Next, how to carry out covering formation of the coat m of an Ti-N system compound on Substrate c is explained using the equipment shown in aforementioned drawing 8.

[0006] First, passing Ar gas for electric discharge to the hollow cathode electron gun f, after carrying out evacuation of the inside of the vacuum membrane formation room a by vacuum pump b, the direct current voltage of number 10- number 100V is impressed from the power supply g for electric discharge between the hollow cathode electron gun f and Haas d, and it discharges among [ f and d ] both.

[0007] Then, a lot of electron beam h generated by hollow cathode electric discharge within the hollow cathode electron gun f is irradiated by metal material [ in metal evaporation-source Haas d ] e (Ti), melting of Ti of the metal material e is carried out by heating by the electron impact, and it generates Ti neutral beam (Ti steam) by it. The part comes to be ionized by the shock with Ar ion in which this Ti neutral beam (Ti steam) is formed of electron beam h and hollow cathode electric discharge. Since the negative direct-current bias voltage of several 10 V is impressed to Substrate c by bias-power-supply k in that case, it is accelerated, and with Ti neutral beam (Ti steam), incidence of the ionized Ti ion beam is carried out to Substrate c, and it forms Ti film in the front face of Substrate c.

[0008] Although Nnozzle 2 gas is passed simultaneously with irradiation of Ti ion beam and Ti neutral beam from i when forming the Ti-N film m on Substrate c, this N<sub>2</sub> gas reacts with Ti ion beam and Ti neutral beam which the part is ionized like Ti steam and carry out incidence to the front face of Substrate c with N<sub>2</sub> neutral beam and which carry out incidence simultaneously there, and comes to form the Ti-N film m.

[0009]

[Problem(s) to be Solved by the Invention] It is become to about 2200 by the Ti-N film, and has become [ in / the VIKKASU degree of hardness (Hv) / as a degree of hardness of the film m on the substrate c formed of PVD or CVD ] about 3700 by the Ti-C film. Moreover, considering the adhesion between the formed Ti-N film, between substrates and a Ti-C film, and a substrate, the Ti-N film and Ti-C film which were formed are whether it only deposits on the front face of a substrate, or slight mixing is performed with the substrate surface layer by the ion bombardment and thermal diffusion by bias. Therefore, the adhesion of an Ti-N film, a Ti-C film, and a substrate is not so good.

[0010] As shown in the \*\* type view shown in drawing 9 (A), the Ti-N film m has deposited the sample which coated the Ti-N film m on Substrate c with equipment conventionally which is shown in drawing 8 bordering on a clear interface on Substrate c.

And when friction / sliding partner material is forced to the sample of the drawing 9 (A) \*\*, when [ hard and ] the adhesion of the Ti-N film m is small, as the Ti-N film m on Substrate c shows drawing 9 (B), some Ti-N films m exfoliate from the front face of Substrate c, and it does not function as abrasion resistance and sliding \*\*\*\*. Among drawing 9 (B), n shows friction / sliding partner material, and partner material and a film scratch it at the time of actual use, or it is equivalent to the partner material at the time of friction and an abrasion test (indenter).

[0011] Thus, when coating of the wear-resistant film to the moving part of tool material or a precision mechanical equipment etc. and sliding \*\*\*\* is considered, it is necessary to raise the life of a tool and parts, and a performance by improvement of the adhesion to the substrate of a coating film in the meaning which suppresses hard-izing of a coating membrane layer, and ablation of a film.

[0012] The purpose of this invention is to offer the formation method of the nature compound of Ti-rare-earth-elements-N system superhard which has a degree of hardness more than the Ti-N film of coating material used conventionally, and a Ti-C film, and a sliding property, and the nature compound film excellent in the adhesion to a substrate top of Ti-rare-earth-elements-N system superhard.

[0013]

[Means for Solving the Problem] This invention persons paid their attention to the atomic radius (single bond radius) indicated by the chemical bond theory (revised edition) [polling work, a Masao Koizumi translation, and Kyoritsu shuppan Co., Ltd. May 20, 1962 amendment 1 \*\*\*\*], as a result of inquiring wholeheartedly that the aforementioned purpose should be attained.

[0014] Furthermore, when it states in detail, as for rare earth elements, the atomic radius of the large value is Dy:1.60A and Y:1.62A as opposed to Ti:1.32A compared with transition metals, such as Ti.

[0015] When rare earth elements are made to replace by Ti site in an Ti-N crystal matrix, the increase in the degree of hardness of Ti-X-N (a dissolution element and here, X is rare earth elements) can be expected by grid distortion by existence of an atom with a big radius.

[0016] On the other hand, it is supposed that the Hume Rothery rule [Hume-Rothery's Rule] generally given experientially is followed whether an alloying element carries out replaced type dissolution.

[0017] and the Ti-M system (M -- rare earth elements --) which took electronegativity along the vertical axis and took the atomic radius along the horizontal axis drawing (Ln shows a lanthanoids among drawing) showing the DAKEN Gary plot showing a transition-metals element [Darken-Gurry's polt] -- in detail Dissolution range [ according to drawing 1 ] according [ the circle centering on Ti (the atomic radius of Ti is 1.32A and electronegativity is 1.4) ] to this Hume Rothery rule (a difference with Ti less than \*\*15% by the atomic radius) It is less than \*\*0.4% in electronegativity, and although the rare earth elements currently mentioned as an element included in Ti-N by this invention go into within the limits mostly in electronegativity, they are over the range in the direction of + in the atomic radius. Therefore, the knowledge of becoming Ti-X-N the non-balancing compound containing such rare earth elements (X expressing rare earth elements), and being able to form the high coating film of a degree of hardness was carried out.

[0018] The nature compound film of Ti-rare-earth-elements-N system superhard and its formation method of this invention are made based on the aforementioned knowledge, and the thin film of the aforementioned hard compound is characterized by to be the thin film of the compound carried out 0.5-20 atom % content about rare earth elements into the constituent which consists of Ti and N in the thin film which consists of the nature compound of Ti-N system superhard with which the nature compound film of Ti-rare-earth-elements-N system superhard was formed on the substrate.

[0019] And into the constituent which consists of Ti and N, when a content does not fulfill 0.5 atom %, hardening by dissolution is eye an inadequate hatchet, and when a content exceeded 20 atom %, the amount of content \*\*\*\* rare earth elements was made into 0.5 to 20 atom %, because the degree of hardness of the compound film obtained was saturated.

[0020] The formation method of the nature compound film of Ti-rare-earth-elements-N system superhard The high-speed ion beam from the steamy metal and the source of an ion beam from a metal evaporation source is irradiated at a substrate. It is the ion mixing method make the nature compound film of superhard form on this substrate. One sort or two or more elements are made into an ion beam among Ti and N which constitute the nature compound of superhard, and rare earth elements, and it is characterized by carrying out compound irradiation of the beam of the gas which contains metallic fumes or these elements for the remaining elements at this substrate, and forming the nature compound film of superhard.

[0021]

[Function] As compared with Ti, since the atomic radius is large, distortion arises in the crystal lattice of the compound compounded by making rare earth elements newly contain in the constituent which consists of Ti and N, and a degree of hardness increases rare earth elements to it.

[0022] By irradiating the high-speed ion beam from an ion beam at a substrate, quenching of the alloy element on a substrate front face is carried out from the non-equilibrium excited by the high energy, and a non-balancing compound is compounded.

[0023] Moreover, by irradiating one or two or more elements to up to a substrate in the form of an ion beam among Ti, N, and rare earth elements Cutting of combination [ in the interface portion between a Ti-rare-earth-elements-N compound film and a substrate ] of Ti, N, rare earth elements, and a substrate composition element by the ion irradiation shock, A mixing operation of knock-on pouring of an atom, a thermal effect, etc. is received, decomposition and reunion are performed, the element of a compound film is mutually mixed with a substrate continuously, and the interface mixing layer which connects a substrate and a compound film firmly is formed. The adhesion of a substrate and a compound film improves by existence of this interface mixing layer.

[0024]

[Example] According to an accompanying drawing, the example of this invention is explained below.

[0025] Drawing 2 shows one example of the film formation equipment for forming the nature compound film of Ti-rare-earth-elements-N system superhard of this invention, one is a vacuum membrane formation room among drawing, and the vacuum membrane formation room 1 is connected to the vacuum pump 2 through the pressure regulation bulb 3. Moreover, in the metal which 4 coats, the substrate made from ceramics, the substrate electrode holder with which 5 holds a substrate 4, and 6, metal evaporation-source Haas and 7 show Ti metal with which as for the ion source and an ion accelerator, and 9 a quantity-of-gas-flow regulator and 11 evaporate in an ion beam and 10, and a gas introduction nozzle and 12 evaporate [ Ti metallic fumes (neutral beam) and 8 ] a gas beam and 13, and 14 shows the heater for substrate heating.

[0026] Next, the concrete example of formation of the nature compound film of Ti-rare-earth-elements-N system superhard on a substrate is explained with the example of comparison using the aforementioned equipment.

[0027] In example 1 this example, the substrate 4 was used as steel materials (JIS-SUS-440C, HRC >60) with a diameter [ of 40mm ] x thickness of 5mm, and the rare earth elements contained in Ti and N were made into the dysprosium (Dy).

[0028] First, the air in the vacuum membrane formation room 1 was discharged with the vacuum pump 2, and the pressure was set as the degree of high vacuum of ten to 5 Pa. And in the vacuum membrane formation room 1, NH<sub>3</sub> gas which adjusted the flow rate to 2.0SCCM(s) with the quantity-of-gas-flow regulator 10 was introduced as a gas beam 12 from the gas introduction nozzle 11, the opening of the pressure regulation bulb 3 was adjusted, and the pressure in the vacuum membrane formation room 1 was maintained to 4x10 to 4 Pa.

[0029] The steel substrate 4 held at the heater 14 for substrate heating at the substrate electrode holder 5 was heated, and it maintained at 300 degrees C. In this state, the Ti metal 13 in metal evaporation-source Haas 6 was fused, and was evaporated by electron beam heating, and it irradiated on the substrate 4 as Ti metallic fumes (neutral beam) 7.

[0030] The ion beam 9 of the dysprosium (Dy) pulled out from the ion source and the ion accelerator 8 simultaneously with it was irradiated on the substrate 4. In addition, the evaporation rate to substrate 4 front face of the Ti metal 13 was carried out in 2.0A/second. Moreover, energy of the ion beam of a dysprosium (Dy) was made to 30keV(s), and current density was made into 5.6microA/cm<sup>2</sup>.

[0031] Operation of the aforementioned conditions was continuously performed until the thin film 15 of the nature compound of Ti-Dy-N system superhard formed on a substrate 4 was set to 1 micrometer (refer to drawing 7 (A)).

[0032] When the crystal structure of the formed nature compound film of Ti-Dy-N system superhard was investigated by X-ray diffraction, it was the polycrystal of the same crystal system (NaCl type) as Ti-N which has a lattice constant near Ti-N.

[0033] Moreover, the result of the lattice constant of the crystal for which it asked from the X-ray diffraction angle of the NaCl type crystal (200) side of the nature compound film of Ti-Dy-N system superhard was shown in drawing 3 as a plot sign A. In addition, the atomic ratio of the horizontal axis in drawing 3 was taken as Dy/(Ti+Dy) calculated by EPMA from film composition.

[0034] Moreover, the Ti-Dy-N compound took the form of N<sub>y</sub> (Ti<sub>1-x</sub>, Dy<sub>x</sub>) "x=Dy/(Ti+Dy) atomic ratio, and y=0.67-1.13 are expressed among a formula", and the value (based on a BEGASU rule) of the lattice constant at the time of assuming that it was replaced ideal for Ti site under crystal of Dy was shown as a weighted-solidity line G in drawing 3.

[0035] Moreover, the VIKKASU degree of hardness (Hv) of the formed nature compound film of Ti-Dy-N system superhard was measured by the VIKKASU hardness tester, and the plot sign A showed the result to drawing 4. In addition, the atomic ratio of the horizontal axis in drawing 4 was taken as Dy/(Ti+Dy) calculated by EPMA from film composition.

[0036] Moreover, friction and the abrasion test in the inside of the vacuum of the formed nature compound film of Ti-Dy-N system superhard were performed, and the measurement result was shown in drawing 5 as a curve H. In addition, friction and an abrasion test rotate a test sample, is performed by the examining method which pushes a partner material ball against the periphery portion of a fixed distance from the center of rotation and which is generally called a pin-on disc method, and evaluates friction / wear property by change of coefficient of friction between the sample-partner material at the time of rotation, and the wear degree of the periphery friction truck section. In partner material, phi7mm SUS440C steel (HRC > 60) and the distance from the center of rotation made [ the test condition ] 7.25mm and movement linear velocity 9.1m a part for /and 514g of forcing loads.

[0037] Moreover, the cross-section configuration of a friction truck when 64 minutes pass after the test start of the friction and the abrasion test in the inside of the vacuum of the nature compound film of Ti-Dy-N system superhard was shown in drawing 6 (A) as a curve I, and the vertical-axis change state of this curve I was expanded, and this was shown in drawing 6 (B) as a curve J.

[0038] Except having changed 2.0 - 6.0SCCM and Dy ion current density, and having changed [ the flow rate of example 2 - 5NH<sub>3</sub> gas ] the incidence ratio of Ti, Dy, and N for Ti evaporation rate in the 1.3-3.0A [/second ] condition range, the nature compound film 15 of Ti-Dy-N system superhard was formed on the substrate 4 by the same method [ A/cm / 13.0-23.0micro ] as the aforementioned example 1, and this was made into examples 2, 3, 4, and

[0039] the lattice constant of a crystal [ angle / X-ray diffraction / of the NaCl type crystal (200) side of the nature compound film of Ti-Dy-N system superhard of each formed example ] -- the same method as an example 1 -- asking -- the result -- the plot sign B and the example 3 were shown for the example 2, and the plot sign D and the example 5 were shown for the plot sign C and the example 4 in drawing 3 as a plot sign E

[0040] Moreover, the VIKKASU degree of hardness (Hv) of the nature compound film of Ti-Dy-N system superhard of each formed example was measured by the same method as an example 1, the plot sign B was shown for the example 2, and the plot sign D and the example 5 were shown [ the result ] for the example 4 in drawing 4 as a plot sign E.

[0041] In addition, when each conditions of NH<sub>3</sub> quantity of gas flow (SCCM) in examples 1-5, Dy ion current density ( $\mu\text{A}/\text{cm}^2$ ), and Ti evaporation rate (Å/second) are shown, it is as in the following table 1.

[0042]

[Table 1]

	NH <sub>3</sub> ガス流量 (SCCM)	Dy イオン電流密度 ( $\mu\text{Å}/\text{cm}^2$ )	Ti 蒸着速度 (Å/秒)
実施例 1	2.0	5.6	2.0
実施例 2	2.0	13.0	2.5
実施例 3	6.0	23.0	1.3
実施例 4	3.9	23.0	2.7
実施例 5	3.9	23.0	3.0

[0043] Conventionally which is shown in example of comparison 1 drawing 8, the Ti-N film m of 1 micrometer of thickness was formed using the HCD ion plating system on Substrate (steel materials with a diameter x thickness of 5mm [JIS-SUS-440C, HRC > 60]) c, from the X-ray diffraction angle of the NaCl type crystal (200) side of the formed Ti-N film m, it asked for the lattice constant of a crystal by the same method as an example 1, and the result was shown in drawing 3 as a plot sign F

[0044] Moreover, the VIKKASU degree of hardness (Hv) of the formed Ti-N film was measured by the same method as an example 1, and the result was shown in drawing 4 as a plot sign F.

[0045] Moreover, friction and the abrasion test in the inside of the vacuum of the formed Ti-N film were performed by the same method as an example 1, and the measurement result was shown in drawing 5 as a curve S. Moreover, the cross-section configuration of the friction truck at friction and the abrasion test end (test end time is 64 minutes) time was shown in drawing 6 (C) as a curve T.

[0046] about [ the forecast (the weighted-solidity line G of drawing 3) of the lattice constant according to the actual measurement of the lattice constant of the example of this invention, and a BEGAZU rule so that clearly from drawing 3, and ] -- it turns out that I am doing one On the other hand, the lattice constant value of the example 1 of comparison by the conventional method was 4.24Å.

[0047] Moreover, in the example 1 of comparison, the degree of hardness was as low as 1800 to a VIKKASU degree of hardness (Hv) increasing in this invention example with the increase in the content of Dy in the nature compound of Ti-Dy-N system superhard so that clearly from drawing 4, and a degree of hardness exceeding 4000 at the maximum. Therefore, it understood that the degree of hardness of the film obtained by making rare earth elements contain in the constituent which consists of Ti-N may be made to increase.

[0048] Moreover, coefficient of friction shows a low value 0.04 order until it results in friction, and abrasion test time 182 minutes in this invention example so that clearly from drawing 5 and drawing 6. And most wear on the front face of a sample is not observed, but there is about 500-1000Å of dry areas on the front face of a sample like drawing 6 (B). Compared with 1 micrometer (10000Å) of thickness of the nature compound film of Ti-Dy-N system superhard, are small. In the example 1 of comparison, coefficient of friction is as larger as 0.6 to having not worn most substrates out than friction and the early stages of an abrasion test. It does not obtain. and a big change accepts to coefficient of friction in 47 minutes after a test start -- having -- test time 64 minutes -- an examination -- not stopping -- And as for the example 1 of comparison, signs that the Ti-N compound film did not exist in a friction truck, but a substrate was deep and it had received wear in it in test time 64 minutes were observed so that clearly [ in drawing 6 (C) ]. Therefore, in this invention example, it turns out that the film obtained by making rare earth elements contain in the constituent which consists of Ti-N is excellent in abrasion resistance.

[0049] It turns out that the nature compound film of Ti-Dy-N system superhard created in this invention example as mentioned above is equipped with the antifriction and abrasiveness which the smooth friction and sliding surface were obtained by the peeling resistance resulting from the high degree of hardness of the film itself, and the high adhesion to a substrate, and was excellent.

[0050] This is connected with drawing 7 [the \*\* type view of the substrate 4 of an Ti-Dy-N coating sample and the Ti-Dy-N compound film 15 with which drawing 7 (A) was created in the example 1, and the \*\* type view showing the state where drawing 7 (B) forced friction / wear partner material 17 on the Ti-Dy-N compound film 15], and is described.

[0051] The interface of a substrate 4 and the nature compound film 15 of Ti-Dy-N system superhard understands signs that the interface mixing layer 16 which the element of the nature compound film 15 of Ti-Dy-N system superhard is continuously mixed with a substrate 4 mutually, and connects firmly a substrate 4 and the nature compound film 15 of Ti-Dy-N system superhard according to the mixing effect by ion irradiation is formed so that clearly from drawing 7 (A).

[0052] Moreover, the nature compound film 15 of Ti-Dy-N system superhard which was formed on the substrate 4 unlike the conventional Ti-N compound film of drawing 9 (B) so that clearly from drawing 7 (B) is hard. And since the adhesion of the film to a substrate is large, even if friction / wear partner material 17 is strongly forced on the nature compound film 15 of Ti-Dy-N system superhard, the nature compound film 15 of Ti-Dy-N system superhard does not exfoliate from a substrate 4. It turns out that the flat nature of the nature compound film of Ti-Dy-N system superhard is maintained, and it excels in abrasion resistance and sliding nature.

[0053] Although Dy was used as rare earth elements made to contain in the aforementioned example, this invention is not limited to this and you may make it make rare earth elements, such as an yttrium (Y), a lanthanum (La), neodymium (Nd), and a gadolinium (Gd), contain.

[0054] Moreover, although Dy+ was used as an ion beam which irradiates a substrate among the aforementioned example and NH3 beam was used as Ti gas and a gas (molecule) beam as a neutral beam this invention is not what is limited to this. as an ion beam Ti+, As N+, N2+, rare-earth-elements ion, and a neutral beam, rare earth elements, such as Dy, In case TiCl4, TiBr4, TiI4, and N2 gas are mentioned as N atom or N radical beam, and a gas beam and a substrate is irradiated, it is independent, respectively. Or you may make it irradiate with the compound beam combined with any of the aforementioned ion beam, the aforementioned neutral beam, or the aforementioned gas beam they are with two or more mixed beams if needed.

[0055]

[Effect of the Invention] Thus, when based on the nature compound film of Ti-rare-earth-elements-N system superhard of this invention While distortion arises in a crystal lattice, it becomes Ti-rare-earth-elements-N a non-balancing compound and a degree of hardness increases as compared with the conventional Ti-N system compound film by the big rare earth elements of the atomic radius contained in the constituent which consists of Ti and N Since it has the adhesion which was excellent to the substrate, the substrate in which this nature compound film of superhard was formed has effects, such as excelling in the friction sliding and abrasion resistance.

[0056] Moreover, when based on the formation method of the nature compound film of Ti-rare-earth-elements-N system superhard of this invention Since some of Ti and N which constitute the nature compound of superhard, and rare earth elements were irradiated and supplied on the substrate in the form of an ion beam KUENCHI [ the compound element formed on a substrate / equilibrium / non-/ which was excited by the high energy ] Can compound Ti-rare-earth-elements-N of a non-balancing compound on a substrate, and it sets into the interface portion of a Ti-rare-earth-elements-N compound film and a substrate by the ion beam. Intense mixing arises between a film composition element and a substrate composition element, and a film composition element and a substrate composition element are mutually mixed with this compound film continuously in the interface portion of a substrate by this mixing. Since the interface mixing layer which connects both firmly is formed, as compared with a conventional method, a degree of hardness is high and it is effective in the ability to offer the method of forming very easily the nature compound film of superhard which was excellent in adhesion to the substrate on a substrate.

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DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] The DAKEN Gary plot view of an Ti-M (M expresses rare-earth-elements and transition-metals element) system,

[Drawing 2] Outline explanatory drawing of one example of the equipment for forming the nature compound film of

Ti-rare-earth-elements-N system superhard of this invention,

[Drawing 3] The weighted-solidity view showing the relation of the membranous atomic ratio ( $Dy/Ti+Dy$ ) and lattice constant which were formed in this invention example and the example of comparison,

[Drawing 4] The weighted-solidity view showing the membranous atomic ratio ( $Dy/Ti+Dy$ ) and the relation of a VIKKASU degree of hardness which were formed in this invention example and the example of comparison,

[Drawing 5] The ultimate-lines view showing the relation of the test time of the pin-on disk friction test of a film sample and coefficient of friction which were formed in this invention example and the example of comparison,

[Drawing 6] It is the cross section of friction / wear truck of the friction test sample after the same time progress at the time of the pin-on disk friction test of the film sample formed in this invention example and the example of comparison, and, for (A) and (B), this invention example and (C) are an example of comparison.

[Drawing 7] It is the film and the \*\* type view of a substrate which were formed in this invention example, and (A) forces the \*\* type view after film formation against a film, (B) forces partner material, and it is a \*\* type view at the time of friction / sliding state.

[Drawing 8] Outline explanatory drawing of the equipment for forming the conventional Ti-N system compound film,

[Drawing 9] It is the film and the \*\* type view of a substrate which were formed with conventional-method equipment, and (A) forces the \*\* type view after film formation against a film, (B) forces partner material, and it is a \*\* type view at the time of friction / sliding state.

[Description of Notations]

1 Vacuum membrane formation room 4 A substrate, 6 Metal evaporation-source Haas 7 Ti metallic fumes (neutral beam), 8 The ion source and ion accelerator 9 An ion beam, 10 Gas introduction nozzle 11 A gas beam, 12 Gas beam 13 Ti metal, 15 Ti-rare-earth-elements-N system compound film.

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CLAIMS

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[Claim(s)]

[Claim 1] It is the nature compound film of Ti-rare-earth-elements-N system superhard characterized by being the thin film of the compound carried out 0.5-20 atom % content about rare earth elements in the constituent with which the thin film of the aforementioned hard compound consists of Ti and N in the thin film which consists of the nature compound of Ti-N system superhard formed on the substrate.

[Claim 2] The high-speed ion beam from the steamy metal and the source of an ion beam from a metal evaporation source is irradiated at a substrate. It is the ion mixing method make the nature compound film of superhard form on this substrate. One sort or two or more elements are made into an ion beam among Ti and N which constitute the nature compound of superhard, and rare earth elements. The formation method of the nature compound film of Ti-rare-earth-elements-N system superhard characterized by carrying out compound irradiation of the beam of the gas which contains metallic fumes or these elements for the remaining elements at this substrate, and forming the nature compound film of superhard.

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Dec 14, 1993

DERWENT-ACC-NO: 1994-022727  
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TITLE: Ultra:hard film for cutting tools - comprises titanium@, nitrogen and rare earth metal additive which may be introduced by ion beam irradiation

PATENT-ASSIGNEE: ULVAC CORP (ULVA)

PRIORITY-DATA: 1992JP-0133991 (May 26, 1992)

## PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE	PAGES	MAIN-IPC
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PUB-NO	APPL-DATE	APPL-NO	DESCRIPTOR
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JP 3205943B2		JP 5330956	Previous Publ.

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ABSTRACTED-PUB-NO: JP 05330956A  
BASIC-ABSTRACT:

Film comprises a cpd. contg. Ti and N as main components and rare earth element as an additive. The additive content is 0.5-20 atom.% and may be added by irradiating the element with an ion beam.

USE - For making cutting tools.

ABSTRACTED-PUB-NO: JP 05330956A  
EQUIVALENT-ABSTRACTS:

CHOSEN-DRAWING: Dwg.0/7

DERWENT-CLASS: L02 M13  
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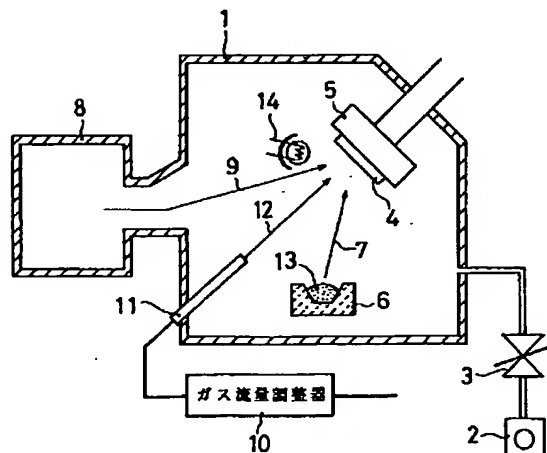
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(54)【発明の名称】 Ti-希土類元素-N系超硬質化合物膜およびその形成方法

(57) 【要約】

【目的】 ヴィッカーズ硬度が3000以上で、基板に対して密着性が優れ、化合物の薄膜が形成された材料の摩擦・摺動および耐摩耗性を向上させたTi—希土類元素—N系超硬質化合物膜と、その形成方法。

【構成】 Ti および N から成る組成物中に希土類元素を 0.5 ～ 20 原子% 含む化合物から成る Ti - 希土類元素 - N 系超硬質化合物膜。超硬質化合物を構成する Ti、N および希土類元素のうち 1 種または複数の元素を含むガスのビームを基板に複合照射するイオンミキシング法により基板上に Ti - 希土類元素 - N 系超硬質化合物膜を形成する方法。



## 【特許請求の範囲】

【請求項1】 基板上に形成されたTi-N系超硬質化合物から成る薄膜において、前記硬質化合物の薄膜はTiおよびNから成る組成物中に希土類元素を0.5～20原子%含有した化合物の薄膜であることを特徴とするTi-希土類元素-N系超硬質化合物膜。

【請求項2】 金属蒸発源からの蒸気金属およびイオンビーム源からの高速イオンビームを基板に照射して、該基板上に超硬質化合物膜を形成させるイオンミキシング法であって、超硬質化合物を構成するTi、Nおよび希土類元素のうち1種または複数の元素をイオンビームとし、残りの元素を金属蒸気、或いはこれら元素を含むガスのビームを該基板に複合照射して超硬質化合物膜を形成することを特徴とするTi-希土類元素-N系超硬質化合物膜の形成方法。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】本発明は、Ti-希土類元素-N系超硬質化合物膜およびその形成方法に関し、更に詳しくは、金属産業や、機械・装置産業で使用する工具や、各種装置に用いられる構成部品や、摺動材料表面上にコーティング膜を形成し、材料表面の硬度、耐摩耗性、および摺動特性の性能を改善したTi-希土類元素-N系超硬質化合物膜および該膜をイオンミキシング法を用いて形成する方法に関する。

## 【0002】

【従来の技術】従来、この種の金属等の基板上に形成された硬質・耐摩耗性および摺動性コーティング膜としては、PVD法、或いはCVD法により基板上に形成されたTi-N、Ti-C等の化合物の薄膜が知られている。

【0003】これらTi-N、Ti-C等の化合物の薄膜はほとんど同様の方法で形成されるが、前記方法のうち、PVD法コーティングの代表例として、従来より広く行われているホローカソード放電(HCD)-イオンプレーティング法による基板上へのTi-N膜の形成の場合について説明すれば次のようになる。

【0004】まず、PVD法に用いる装置について説明する。図8はHCDイオンプレーティング装置を示すものであり、図中、aは真空成膜室を示し、該真空成膜室a内は真空ポンプbに接続されている。また、cはコーティングに供される主として金属材料製の基板、dは金属蒸発源ハース、eは蒸発させる金属材(ここではTi)、fはホローカソード電子銃、gはホローカソード電子銃fと金属蒸発源ハースdに電圧を印加する放電用電源、hは電子ビーム、iはN<sub>2</sub>ガスを流すノズル、jは一部イオン化されたN<sub>2</sub>ガス、kは基板cに電圧を印加するバイアス電源を示す。

【0005】次に、前記図8に示す装置を用いて、基板c上にTi-N系化合物の被膜mを被覆形成する方法に

ついて説明する。

【0006】まず、真空成膜室a内を真空ポンプbで真空排気した後、ホローカソード電子銃fに放電用Arガスを流しながら、ホローカソード電子銃fとハースdとの間に数10～数100Vの直流電圧を放電用電源gより印加して両者間f、dに放電を行う。

【0007】そのとき、ホローカソード電子銃f内でのホローカソード放電により生成する多量の電子ビームhは金属蒸発源ハースd内の金属材e(Ti)に照射され、その電子衝撃による加熱により、金属材eのTiは溶融され、Ti中性ビーム(Ti蒸気)を発生する。このTi中性ビーム(Ti蒸気)は電子ビームhおよびホローカソード放電により形成されるArイオンとの衝撃により、その一部がイオン化されるようになる。その際、基板cには数10Vの負の直流バイアス電圧がバイアス電源kによって印加されているので、イオン化されたTiイオンビームは加速され、Ti中性ビーム(Ti蒸気)と共に、基板cに入射して、基板cの表面にTi膜を形成する。

【0008】基板c上にTi-N膜mを形成する場合は、ノズルiよりN<sub>2</sub>ガスをTiイオンビームおよびTi中性ビームの照射と同時に流すが、このN<sub>2</sub>ガスはTi蒸気と同じようにその一部がイオン化され、基板cの表面にN<sub>2</sub>中性ビームと共に入射し、そこで同時に入射するTiイオンビームおよびTi中性ビームと反応して、Ti-N膜mを形成するようになる。

## 【0009】

【発明が解決しようとする課題】PVD法、またはCVD法により形成された基板c上の膜mの硬度としては、ヴィッカース硬度(Hv)においてTi-N膜で約2200、Ti-C膜で約3700となっている。また、形成されたTi-N膜と基板の間、Ti-C膜と基板の間の密着性を考えると、形成されたTi-N膜やTi-C膜は基板の表面上に単に堆積するか、或いはバイアスによるイオン衝撃や熱拡散によって基板表面層と僅かなミキシングが行われているかである。そのため、Ti-N膜やTi-C膜と基板との密着性は余りよくない。

【0010】図8に示す従来装置により基板c上にTi-N膜mをコーティングを行った試料は図9(A)に示す模式図のように基板c上にTi-N膜mが明確な界面を境にして堆積している。そして、図9(A)示の試料に対し、摩擦・摺動相手材を押し付けた際、基板c上のTi-N膜mが硬く、かつTi-N膜mの密着性が小さい場合は図9(B)に示すようにTi-N膜mの一部が基板cの表面から剥離し、耐摩耗性、摺動性膜として機能しない。図9(B)中、nは摩擦・摺動相手材を示し、実際の使用時には相手材、膜の引っ掻き、或いは摩擦・摩耗試験時の相手材(圧子)に相当するものである。

【0011】このように、工具材または精密機器の摺動

部品等への耐摩耗性膜、および摺動性膜のコーティングを考えた場合、コーティング膜層の硬質化、並びに膜の剥離を抑える意味で、コーティング膜の基板への密着性の改善により工具、部品の寿命、性能を向上させることが必要となる。

【0012】本発明の目的は、従来用いられているコーティング材料のTi-N膜、Ti-C膜以上の硬度、摺動特性を有するTi-希土類元素-N系超硬質化合物および、基板上への密着性に優れたTi-希土類元素-N系超硬質化合物膜の形成方法を提供することにある。

【0013】

【課題を解決するための手段】本発明者らは、前記目的を達成すべく鋭意検討した結果、化学結合論（改訂版）〔ボーリング著、小泉正夫訳、共立出版（株） 1962年5月20日改定1刷発行〕に記載されている原子半径（一重結合半径）に着目した。

【0014】更に詳細に述べると、希土類元素はその原子半径がTi等の遷移金属に比べて大きい、その値はTi: 1.32Åに対し例えばDy: 1.60Å、Y: 1.62Åである。

【0015】Ti-N結晶マトリックス中のTiサイトに希土類元素を置換させた場合は、半径の大きな原子の存在による格子歪みによりTi-X-N（Xは固溶元素、ここでは希土類元素）の硬度の増加が期待できる。

【0016】一方、添加元素が置換型の固溶をするかどうかは一般に、経験的に与えられるヒューム・ロザリー則〔Hume-Rothery's Rule〕に従うとされている。

【0017】そして、縦軸に電気陰性度、横軸に原子半径をとったTi-M系（Mは希土類元素、遷移金属元素を表す）のダーケン・ガリーブロット〔Darken-Gurry's plot〕を示す図（図中、Lnはランタノイド元素を示す）、詳しくは、図1によると、Ti（Tiの原子半径は1.32Å、電気陰性度は1.4である）を中心とする円がこのヒューム・ロザリー則による固溶範囲（Tiとの差が原子半径で±15%以内、電気陰性度で±0.4%以内）であり、本発明でTi-Nに含ませる元素として挙げている希土類元素は電気陰性度においてほぼ範囲内に入るものの、原子半径では+方向に範囲を超えるもの（約+20%）となっている。従ってこのような希土類元素を含有するTi-X-N非平衡化合物（Xは希土類元素を表す）となって、硬度の高いコーティング膜を形成することが出来ることを知見した。

【0018】本発明のTi-希土類元素-N系超硬質化合物膜およびその形成方法は、前記知見に基づいてなされたものであり、Ti-希土類元素-N系超硬質化合物膜は、基板上に形成されたTi-N系超硬質化合物から成る薄膜において、前記硬質化合物の薄膜はTiおよびNから成る組成物中に希土類元素を0.5～20原子%含有した化合物の薄膜であることを特徴とする。

【0019】そして、TiおよびNから成る組成物中に

含有せる希土類元素量を0.5～20原子%としたのは、含有量が0.5原子%に満たない場合は固溶による硬化が不十分なためであり、また含有量が20原子%を超えた場合は得られる化合物膜の硬度が飽和してくるためである。

【0020】Ti-希土類元素-N系超硬質化合物膜の形成方法は、金属蒸発源からの蒸気金属およびイオンビーム源からの高速イオンビームを基板に照射して、該基板上に超硬質化合物膜を形成させるイオンミキシング法であって、超硬質化合物を構成するTi、Nおよび希土類元素のうち1種または複数の元素をイオンビームとし、残りの元素を金属蒸気、或いはこれら元素を含むガスのビームを該基板に複合照射して超硬質化合物膜を形成することを特徴とする。

【0021】

【作用】希土類元素はTiに比して原子半径が大きいから、TiおよびNから成る組成物中に希土類元素を新たに含有させることにより合成される化合物の結晶格子に歪みが生じて硬度が増加する。

20 【0022】イオンビームからの高速イオンビームを基板に照射することにより、基板表面上の合金元素は高エネルギーに励起された非平衡状態からクエンチングされ、非平衡化合物が合成される。

【0023】また、Ti、N、希土類元素のうち1つ、或いは複数の元素をイオンビームの形で基板上へ照射することにより、Ti-希土類元素-N化合物膜と基板の間の界面部分でTi、N、希土類元素および基板構成元素がイオン照射衝撃により結合の切断、原子のノックオン注入、熱的効果等のミキシング作用を受け、分解・再結合を行い、基板と化合物膜の元素が互いに連続的に混ざり合い、基板と化合物膜とを強固につなぐ界面ミキシング層を形成する。この界面ミキシング層の存在により基板と化合物膜の密着性は向上する。

【0024】

【実施例】以下添付図面に従って本発明の実施例について説明する。

40 【0025】図2は本発明のTi-希土類元素-N系超硬質化合物膜の形成を実施するための膜形成装置の1例を示すもので、図中、1は真空成膜室であり、真空成膜室1は真空ポンプ2に圧力調整バルブ3を介して接続されている。また、4はコーティングを施す金属製、セラミックス製の基板、5は基板4を保持する基板ホルダー、6は金属蒸発源ハース、7はTi金属蒸気（中性ビーム）、8はイオン源およびイオン加速器、9はイオンビーム、10はガス流量調整器、11はガス導入ノズル、12はガスビーム、13は蒸発させるTi金属、14は基板加熱用ヒーターを示す。

【0026】次に、前記装置を用いて基板上にTi-希土類元素-N系超硬質化合物膜の形成の具体的実施例を比較例と共に説明する。

## 【0027】実施例1

本実施例では基板4を直径40mm×厚さ5mmの鋼材(JIS-SUS-440C, HRC>60)とし、TiおよびNに含有する希土類元素をジスプロシウム(Dy)とした。

【0028】まず、真空成膜室1内の空気を真空ポンプ2により排出して圧力を $10^{-6}$ Paの高真空度に設定した。そして真空成膜室1内にガス流量調整器10で流量を2.0SCCMに調整したNH<sub>3</sub>ガスをガス導入ノズル11よりガスビーム12として導入し、圧力調整バルブ3の開度を調整して真空成膜室1内の圧力を $4 \times 10^{-4}$ Paに維持した。

【0029】基板加熱用ヒーター14で基板ホルダー5に保持された鋼製の基板4を加熱して300℃に維持した。この状態で電子ビーム加熱により金属蒸発源ハース6内のTi金属13を溶融、蒸発させ、Ti金属蒸気(中性ビーム)7として基板4上に照射した。

【0030】それと同時にイオン源およびイオン加速器8から引き出されたジスプロシウム(Dy)のイオンビーム9を基板4上に照射した。尚、Ti金属13の基板4表面への蒸着速度は2.0Å/秒とした。また、ジスプロシウム(Dy)のイオンビームのエネルギーは30keV、電流密度は5.6μA/cm<sup>2</sup>とした。

【0031】前記条件の操作を基板4上に形成されるTi-Dy-N系超硬質化合物の薄膜15が1μmとなるまで継続して行った(図7(A)参照)。

【0032】形成されたTi-Dy-N系超硬質化合物膜の結晶構造をX線回折で調べたところTi-Nに近い格子定数を有するTi-Nと同一の結晶系(NaCl型)の多結晶であった。

【0033】また、Ti-Dy-N系超硬質化合物膜のNaCl型結晶(200)面のX線回折角より求めた結晶の格子定数の結果を図3にプロット記号Aとして示した。尚、図3における横軸の原子比は膜組成よりEPM Aで求めたDy/(Ti+Dy)とした。

【0034】また、Ti-Dy-N化合物が(Ti<sub>1-x</sub>Dy<sub>x</sub>)N<sub>y</sub>「式中、 $x = Dy / (Ti + Dy)$ 原子比、 $y = 0.67 \sim 1.13$ を表わす」の形をとり、Dyが結晶中のTiサイトに理想的に置換されたと仮定した場合の格子定数の値(ペガース則による)を図3中に特性値線Gとして示した。

【0035】また、形成されたTi-Dy-N系超硬質化合物膜のヴィッカース硬度(Hv)をヴィッカース硬

度試験機で測定し、その結果を図4にプロット記号Aで示した。尚、図4における横軸の原子比は膜組成よりEPM Aで求めたDy/(Ti+Dy)とした。

【0036】また、形成されたTi-Dy-N系超硬質化合物膜の真空中での摩擦・摩耗試験を行い、その測定結果を図5に曲線Hとして示した。尚、摩擦・摩耗試験は試験試料を回転させ、回転中心から一定の距離の円周部分に相手材ボールを押し付ける一般にピンオンディスク法と称される試験法で行い、回転運動時の試料-相手材間の摩擦係数の変化、および円周摩擦トラック部の摩耗度合により摩擦・摩耗特性を評価する。試験条件は相手材はφ7mmのSUS440C鋼(HRC>60)、回転中心からの距離は7.25mm、運動線速度は9.1m/分、押し付け荷重514gとした。

【0037】また、Ti-Dy-N系超硬質化合物膜の真空中での摩擦・摩耗試験の試験開始後64分経過したときの摩擦トラックの断面形状を図6(A)に曲線Iとして示し、また同曲線Iの縦軸変化状態を拡大し、これを図6(B)に曲線Jとして示した。

## 【0038】実施例2〜5

NH<sub>3</sub>ガスの流量を2.0〜6.0SCCM、Dyイオン電流密度を13.0〜23.0μA/cm<sup>2</sup>、Ti蒸着速度を1.3〜3.0Å/秒の条件範囲でTi、Dy、Nの入射比を変えた以外は前記実施例1と同様の方法で基板4上にTi-Dy-N系超硬質化合物膜15を形成し、これを実施例2, 3, 4, 5とした。

【0039】形成された各実施例のTi-Dy-N系超硬質化合物膜のNaCl型結晶(200)面のX線回折角より結晶の格子定数を実施例1と同様の方法で求め、その結果を図3に実施例2をプロット記号B、実施例3をプロット記号C、実施例4をプロット記号D、実施例5をプロット記号Eとして示した。

【0040】また、形成された各実施例のTi-Dy-N系超硬質化合物膜のヴィッカース硬度(Hv)を実施例1と同様の方法で測定し、その結果を図4に実施例2をプロット記号B、実施例4をプロット記号D、実施例5をプロット記号Eとして示した。

【0041】尚、実施例1〜5におけるNH<sub>3</sub>ガス流量(SCCM)、Dyイオン電流密度(μA/cm<sup>2</sup>)、Ti蒸着速度(Å/秒)の各条件を示すと下記表1の通りである。

## 【0042】

【表1】

	7		8
	NH <sub>3</sub> ガス流量 ( S C C M )	Dy イオン電流密度 ( μ Å / cm <sup>2</sup> )	Ti 蒸着速度 ( Å / 秒 )
実施例 1	2. 0	5. 6	2. 0
実施例 2	2. 0	13. 0	2. 5
実施例 3	6. 0	23. 0	1. 3
実施例 4	3. 9	23. 0	2. 7
実施例 5	3. 9	23. 0	3. 0

## 【0043】比較例1

図8に示す従来HCDイオンプレーティング装置を用いて基板（直径40mm×厚さ5mmの鋼材〔JIS-SUS-440C, HRC>60〕）c上に膜厚1μmのTi-N膜mを形成し、形成されたTi-N膜mのNaCl型結晶（200）面のX線回折角より結晶の格子定数を実施例1と同様の方法で求め、その結果を図3にプロット記号Fとして示した。

【0044】また、形成されたTi-N膜のヴィッカーズ硬度（Hv）を実施例1と同様の方法で測定し、その結果を図4にプロット記号Fとして示した。

【0045】また、形成されたTi-N膜の真空中での摩擦・摩耗試験を実施例1と同様の方法で行い、その測定結果を図5に曲線Sとして示した。また、摩擦・摩耗試験終了（試験終了時間は64分）時点における摩擦トラックの断面形状を図6（C）に曲線Tとして示した。

【0046】図3から明らかなように本発明の実施例の格子定数の実測値と、ベガーズ則による格子定数の予測値（図3の特性値線G）とはほぼ一致していることが分かった。これに対し従来法による比較例1の格子定数値は4.24Åであった。

【0047】また、図4から明らかなように本発明実施例ではTi-Dy-N系超硬質化合物中のDyの含有量の増加と共に、ヴィッカーズ硬度（Hv）が増加し、最大では硬度が4000を超えるのに対し、比較例1では硬度が1800と低かった。従って、Ti-Nから成る組成物中に希土類元素を含有せしめることにより得られる膜の硬度を増加させ得ることが分かった。

【0048】また、図5および図6から明らかなように本発明実施例では摩擦・摩耗試験時間182分に至るまで摩擦係数は0.04前後と低い値を示し、しかも試料表面の磨耗は殆ど観察されず、図6（B）のように試料表面の荒れは500～1000Å程度あり、Ti-Dy-N系超硬質化合物膜の膜厚1μm（10000Å）に比べ小さく、基板は殆ど摩耗していないのに対し、比較例1では摩擦・摩耗試験初期より摩擦係数は0.6と大きく、しかも試験開始後47分で摩擦係数に大きな変化が認められ、試験時間64分で試験を中止せざるを得ず、しかも図6（C）で明らかなように比較例1は試験時間64分では摩擦トラックにTi-N化合物膜は存在\* 50

\*せず、基板が深く摩耗を受けている様子が観察された。従って、本発明実施例ではTi-Nから成る組成物中に希土類元素を含有せしめることにより得られる膜は耐摩耗性に優れていることが分かった。

【0049】前述のように本発明実施例で作成されたTi-Dy-N系超硬質化合物膜は膜自体の高い硬度、および基板に対する高い密着性に起因する耐剥離性により、平滑な摩擦・摺動面が得られて、優れた耐摩擦・摩耗性を備えていることが分かった。

【0050】このことを図7〔図7（A）は実施例1で作成されたTi-Dy-Nコーティング試料の基板4とTi-Dy-N化合物膜15の模式図、図7（B）はTi-Dy-N化合物膜15に摩擦・摩耗相手材17を押し付けた状態を表す模式図〕と関係づけて述べる。

【0051】図7（A）から明らかなように基板4とTi-Dy-N系超硬質化合物膜15との界面はイオン照射によるミキシング効果により、基板4とTi-Dy-N系超硬質化合物膜15の元素が互いに連続的に混ざり合い、基板4とTi-Dy-N系超硬質化合物膜15とを強固につなぐ界面ミキシング層16が形成されている様子が分かる。

【0052】また、図7（B）から明らかなように図9（B）の従来のTi-N化合物膜とは異なり基板4上に形成されたTi-Dy-N系超硬質化合物膜15は硬く、かつ基板への膜の密着性が高いから、Ti-Dy-N系超硬質化合物膜15に摩擦・摩耗相手材17が強く押し付けられてもTi-Dy-N系超硬質化合物膜15は基板4より剥離することがなく、Ti-Dy-N系超硬質化合物膜の平坦性が保たれて、耐摩耗性、摺動性に優れていることが分かる。

【0053】前記実施例では含有させる希土類元素としてDyを用いたが、本発明はこれに限定されるものではなく、イットリウム（Y）、ランタン（La）、ネオジム（Nd）、ガドリニウム（Gd）等の希土類元素を含有せしめるようにしてもよい。

【0054】また、前記実施例中、基板に照射するイオンビームとしてDy<sup>+</sup>、中性ビームとしてTiガス、ガス（分子）ビームとしてNH<sub>3</sub>ビームを用いたが、本発明はこれに限定されるものではなく、イオンビームとしてはTi<sup>+</sup>、N<sup>+</sup>、N<sub>2</sub><sup>+</sup>、希土類元素イオン、また、

中性ビームとしてはDy等の希土類元素、N原子或いはNラジカルビーム、また、ガスビームとしてはTiCl<sub>4</sub>、TiBr<sub>4</sub>、TiI<sub>4</sub>、N<sub>2</sub>ガスが挙げられ、また、基板に照射する際には夫々単独で、或いは複数の混合ビームで、必要に応じて前記イオンビーム、或いは前記中性ビーム、或いは前記ガスビームの何れかと組合わせた複合ビームで照射するようにしてもよい。

#### 【0055】

【発明の効果】このように本発明のTi-希土類元素-N系超硬質化合物膜によるときは、TiおよびNから成る組成物に含まれる原子半径の大きな希土類元素によって結晶格子に歪みが生じて、Ti-希土類元素-N非平衡化合物となって、従来のTi-N系化合物膜に比して、硬度が増加すると共に、基板に対し優れた密着性を有するので、該超硬質化合物膜が形成された基板は、その摩擦摺動および耐摩耗性に優れる等の効果がある。

【0056】また、本発明のTi-希土類元素-N系超硬質化合物膜の形成方法によるときは、超硬質化合物を構成するTi、Nおよび希土類元素の一部をイオンビームの形で基板上に照射し供給するようにしたので、基板上に形成される化合物元素は高エネルギーに励起された非平衡状態よりクエンチされ、基板上に非平衡化合物のTi-希土類元素-Nを合成出来、また、イオンビームによりTi-希土類元素-N化合物膜と基板との界面部分において、膜構成元素および基板構成元素との間で激しいミキシングが生じ、このミキシングにより該化合物膜と基板の界面部分では膜構成元素と基板構成元素が互いに連続的に混ざり合い、両者を強固につなぐ界面ミキシング層が形成されるから、従来法に比して硬度が高く、基板に対し密着性に優れた超硬質化合物膜を基板上に極めて容易に形成する方法を提供出来る効果がある。

#### 【図面の簡単な説明】

【図1】 Ti-M (Mは希土類元素および遷移金属元

素を表す)系のダーケン・ガリープロット図、

【図2】 本発明のTi-希土類元素-N系超硬質化合物膜の形成を実施するための装置の1例の概略説明図、

【図3】 本発明実施例および比較例で形成された膜の原子比(Dy/Ti+Dy)と格子定数との関係を示す特性値図、

【図4】 本発明実施例および比較例で形成された膜の原子比(Dy/Ti+Dy)とウィッカース硬度の関係を示す特性値図、

10 【図5】 本発明実施例および比較例で形成された膜試料のピンオンディスク摩擦試験の試験時間と摩擦係数との関係を示す特性線図、

【図6】 本発明実施例および比較例で形成された膜試料のピンオンディスク摩擦試験時の同一時間経過後の摩擦試験試料の摩擦・摩耗トラックの断面図であり、

(A)、(B)は本発明実施例、(C)は比較例、

【図7】 本発明実施例で形成された膜と基板の模式図であり、(A)は膜形成後の模式図、(B)は膜に相手材を押し付けて摩擦・摺動状態時の模式図

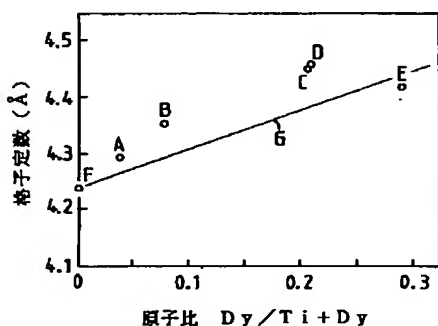
20 【図8】 従来のTi-N系化合物膜の形成を実施するための装置の概略説明図、

【図9】 従来法装置で形成された膜と基板の模式図であり、(A)は膜形成後の模式図、(B)は膜に相手材を押し付けて摩擦・摺動状態時の模式図。

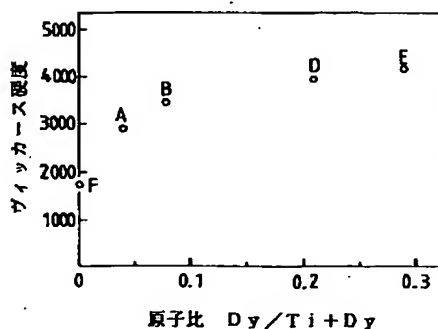
#### 【符号の説明】

1 真空成膜室、 4 基板、 6 金属蒸発源ハース、 7 Ti金属蒸気(中性ビーム)、 8 イオン源およびイオン加速器、 9 イオンビーム、 10 ガス導入ノズル、 11 ガスビーム、 12 ガスビーム、 13 Ti金属、 15 Ti-希土類元素-N系化合物膜。

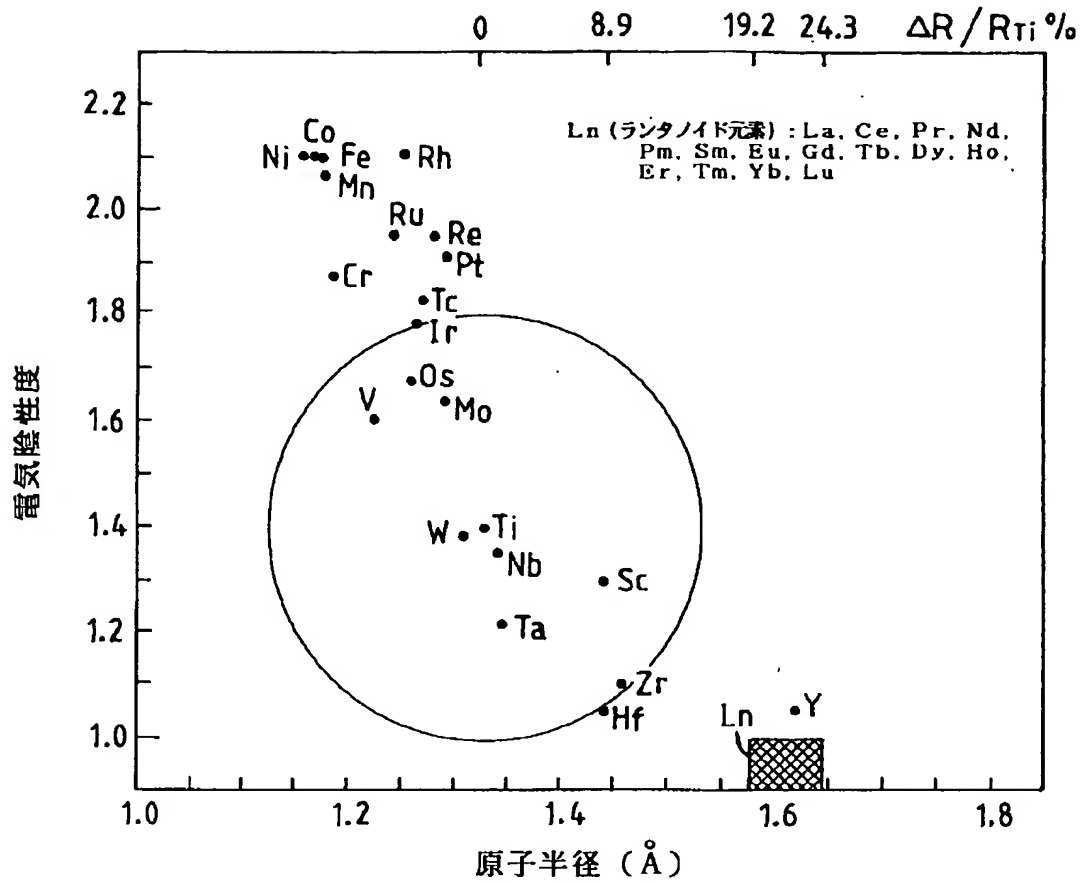
【図3】



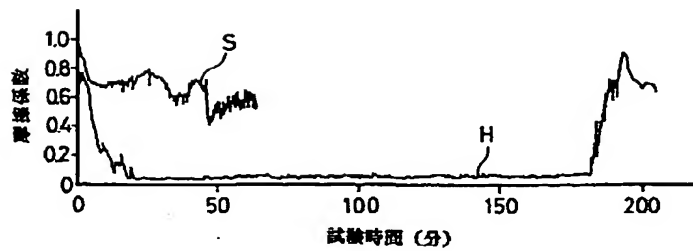
【図4】



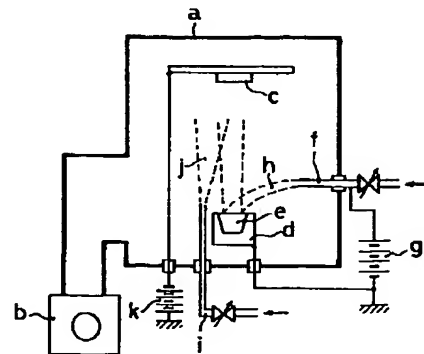
【図1】



【図5】

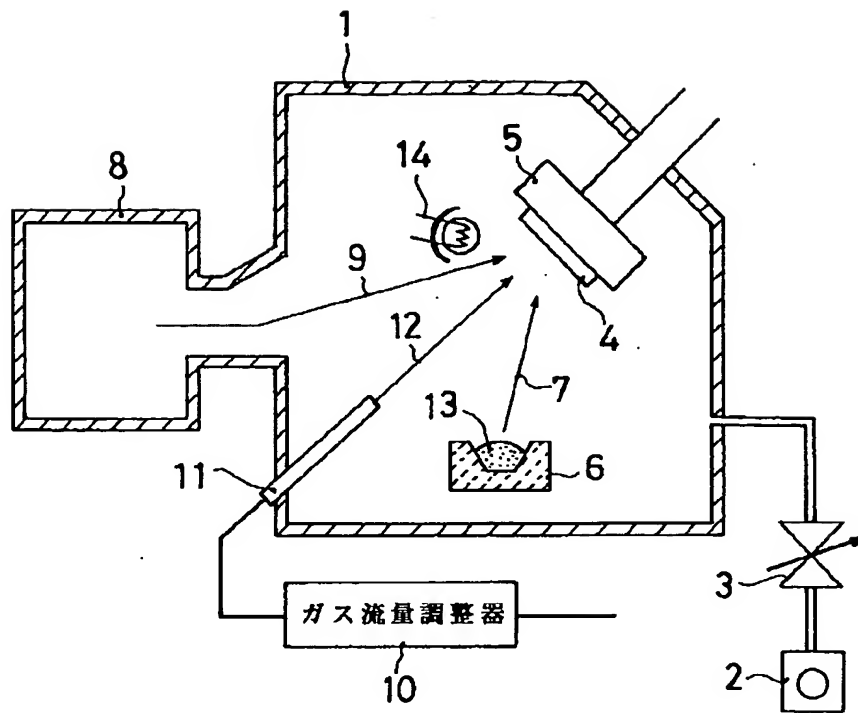


【図8】



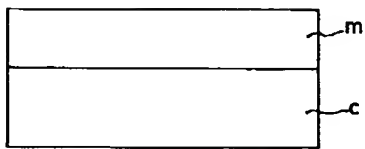


【図2】

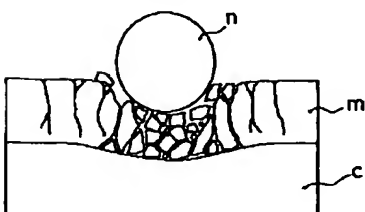


【図9】

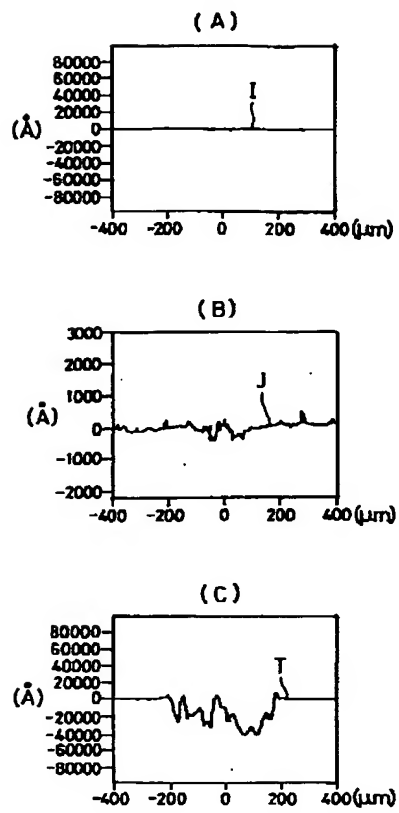
(A)



(B)



【図6】



【図7】

